X-RAY AND PHYSICAL-CHEMICAL STUDIES OF HYDROUS LEAD OXIDE AND NORMAL AND ACTIVE LEAD MONOXIDES

BY

WILLARD PHILIP TYLER

B.S., Oregon State College, 1931

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1938

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I. INTRODUCTION

This investigation was undertaken for the purpose of studying the hydrous oxide of lead and the red and yellow modifications of lead monoxide from the standpoint of their preparation from various sources; the X-ray diffraction patterns of products prepared under different conditions, physical-chemical properties such as catalytic activity and heats of reaction of the products, analysis and any other properties of the substances which would contribute to the total knowledge concerning them.

II. HISTORICAL

The principal reference works concerning the hydrous oxides and oxides are books by Weiser[1] and by Fricke and Hüttig[2]. From these works and cross references found in them most of the information and data for this investigation were obtained. The existing data concerning the lead oxide hydrate include the X-ray diffraction pattern without any attempt to interpret it, methods of preparation, solubility in alkali, isobaric dehydration curves and analyses.

Thorough discussion of the properties of oxides obtained by dehydration of the hydrates of several metals other than lead is to be found in reference[2] and in the work of Fricke[3]. Low temperature dehydration products of the hydrates of these metals showed distorted X-ray patterns, increased catalytic activity and increased heats of reaction over those found for the normally prepared oxides. No work has been reported concerning such properties of the lead monoxides, the yellow orthorhombic form and the red tetragonal modification.

III. THE HYDROUS OXIDE OF LEAD

Preparations of the hydrous oxide of lead were made from lead acetate and ammonium hydroxide, lead acetate and sodium hydroxide and from yellow lead monoxide dissolved in sodium hydroxide, boiled and cooled. The first two products were

coarse white powders, while the third consisted of small white crystals about 0.2 mm. in diameter. The analyses of these preparations were nearly identical, giving the empirical formula $5PbO \cdot 2H_2O$ or $2Pb(OH)_2 \cdot 3PbO$ for the product. The powders contained small quantities of carbon dioxide shown by X-ray data to be in the form of normal lead carbonate probably mixed with basic lead carbonate. X-ray diffraction patterns of these products were taken with a circular, wedge reflection camera, using Cu-Kα radiation. The patterns were identical and an analysis of the spacings of the lines was made. The crystals are monoclinic in all probability. The powder patterns are extremely complex, but by making assumptions concerning the Miller indices of certain observed reflections it was possible to index nearly all of the lines for which the indices h or 1 was zero. Attempts to find the monoclinic angle, β and to index the remaining lines were unsatisfactory. The nearest approximation gave the following values for the unit cell properties: $a_0 = 5.93$ A.U., $b_0 = 4.65$ A.U., $c_0 = 6.36$ A.U., $\beta = 105° 47'$. The measured average density was 7.73. This results in a very rough approximation of one molecule of $5PbO \cdot 2H_2O$ in the unit cell. Final solution will depend upon further work with the very minute crystals.

IV. THE PREPARATION AND PROPERTIES OF NORMAL AND ACTIVE LEAD MONOXIDES

The starting materials for these preparations were the hydrous oxide of lead, normal lead carbonate and basic lead carbonate. The preparations were all obtained by decomposition of the starting materials, usually in vacuum, at temperatures varying from 100° C. to 500° C. The normal yellow lead monoxide was obtained by heating basic lead carbonate to about 700° C. Normal red lead monoxide was obtained by heating normal lead carbonate to temperatures between 350° C. and 500° C. X-ray patterns of these two products were sharp-lined normal patterns.

All decompositions of the hydrates at temperatures below 500° C. showed X-ray patterns of red lead monoxide mixed

with small amounts of the yellow form, the amount of yellow increasing with the temperature of preparation. The same was true of basic lead carbonate decomposition from 240°-500° C., but normal lead carbonate always gave the red form below 500° C.

On every pattern of a product resulting from decomposition at low temperatures close to the decomposition temperature, 100°-200° C. for the hydrate, 240°-300° C. for the carbonates, there appeared a large distortion effect of the lines diffracted by the red form. This distortion was characterized by a broadening and increased diffuseness of reflections from the planes with indices 101, 102, 200, 121, 103 and some smaller spacing planes, while the 110, 002, 112, 113 and 220 reflections remained comparatively sharp. All reflections were considerably less in relative intensity than those on the normal read lead monoxide patterns, the observed intensity decrease varying from 10 to 80 percent, as determined by integrated darkenings measured from microphotometer curves. This distorted product was also characterized by a greater catalytic activity than the normal red lead monoxide as determined by the rate of decomposition of hydrogen peroxide under standardized conditions. The activity was more than doubled by some samples of the active oxide and the difference could not be attributed to particle size differences. A comparison of heat of reaction with concentrated perchloric acid using a simple calorimeter with which results could be checked within 0.33% showed that the active oxide possessed an energy content 1 to 2 % greater than the normal oxide. The energy content of the yellow form and of the hydrate appeared to lie between that of the active and the normal red oxides. All calculations were made by correcting observed heats of reaction for analyzed quantities of carbonate or hydrate impurities. Aging at room temperature for months or at the temperature of preparation for a few days did not change these properties.

V. THEORETICAL DISCUSSION

An attempt to explain the distortion of the active oxides on the basis of directional displacement of the atoms in the lattice was unsuccessful since the indices of reflections which remain

sharp on the patterns preclude all such possibilities, and no lattice stretching was observed. Application of the Debye-Waller effect as described by Compton and Allison[4] and as modified by Zener and Jauncey[5] and Goetz and Jacobs[6] showed that if the observed energy increase in the active oxide was all transformed into thermal agitation with the resulting decrease in intensity of diffracted X-rays, the maximum observed decrease would be less than 2% for high order lines. No other explanation could be found other than the statement that the lattice was probably incompletely formed owing to the conditions of the preparation, and that the energy increase might be localized in "active spots" in this incomplete lattice from which atoms might be missing at random.

An explanation of the formation of yellow lead monoxide from the hydrate and the basic carbonate at temperatures from 250° to 350° below the red to yellow transition temperature was postulated on the basis of the work of Bloom and Buerger on antimony oxide[7]. It is posible that the presence of the hydrate water or even of acetate in small quantities may stabilize the yellow form even though it is produced in a temperature region in which it is supposed to be metastable.

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VITA

The author was born November 9, 1909, in Auburndale, Massachusetts. He received his elementary education there and completed his secondary education at Baltimore Polytechnic Institute, Baltimore, Maryland, in June, 1927. In September of the same year he entered Oregon State College at Corvallis, Oregon, and received the degree of Bachelor of Science in chemical engineering in June, 1931.

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